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UNDERCOOLING AND RATE OF CONDENSATION IN STEAM[1]

BY R. RUEDY[2]

Abstract

The first and most difficult stage in the condensation of water vapour is the increase in the size of the drops until their radius satisfies the Kelvin–Helmholtz equation for the degree of undercooling or supersaturation reached at the temperature T_e of the vapour; the second stage is the increase in size by continued addition of molecules until the vapour pressure $p(\nu)$ of the drop containing ν molecules approaches the pressure p_∞ exerted at the same temperature by a pool of water. A gradual enlargement to visible drops follows. Consideration of the number of collisions of the molecules with the drops forming at the vapour pressure p_e of steam, and the loss of molecules by virtue of the higher vapour pressure of small drops leads to the conclusion that at condensation temperatures between 0° and 50° C. the centres of condensation in the absence of dust or ions contain fewer than a hundred molecules. When the degree of supersaturation corresponds to larger drops, condensation is bound to fail. The conclusion drawn from the theory is confirmed by the values obtained in the tests with flowing steam and with cloud chambers. At higher temperatures larger drops act as nuclei. The growth in the second stage is also extremely rapid, at least until the radius equals in size the wave-length of visible radiation. Water drops of this size, that is, drops that produce coloured diffraction rings, behave as large drops. The heat of condensation may furnish part of the work to be performed against the surface tension.

Introduction

Fifty years ago, C. T. R. Wilson began his famous cloud chamber experiments in the hope of finding an answer to the question: What is the limit to the degree of undercooling that can be obtained without producing condensation in a body of moist air? As, however, the influence that ions or dust exert upon the condensation soon claimed all the attention devoted to the subject, the investigations related to spontaneous condensation remained incomplete, and new studies were required before the results could be more precisely understood. Some of the gaps have since been filled by the investigations carried out mainly on another problem—the flow of steam—in the Department of Mechanical Engineering of Johns Hopkins University (9, 14) and Purdue University (14), the Universities of Rochester (8) and of Pennsylvania (8), and the Stevens Institute of Technology, Hoboken, N.J. (8), as well as at Cambridge (6, 7) and at Oxford (3). Attention was paid in all the tests not only to the degree of undercooling but also to the rate of condensation.

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2 *Research Investigator.*

The material presented in this study was assembled during preparation of a review of the article by C. A. Robb (9).

It is well known that in rapid expansion steam does not condense when saturation has been reached. Instead it continues to expand exactly as in the superheated region, thus becoming undercooled. This condition persists until the water vapour reaches a lower pressure and temperature, where condensation occurs suddenly and a vast number of minute droplets form of such size that in perfect equilibrium their vapour pressure is equal to the pressure exerted by the surrounding steam. According to the Kelvin–Helmholtz equation this pressure is given by

$$\frac{p(n)}{p_\infty} = \epsilon^{\frac{2M\sigma}{\rho RTr_n}},$$

where p_∞ is the vapour pressure measured at the same absolute temperature T over a pool of water (the pressure listed in steam tables), r_n the radius of the drop consisting of n molecules, σ the surface tension, ρ the density, M the molecular weight of water, and finally R the gas constant (Fig. 1). Early in

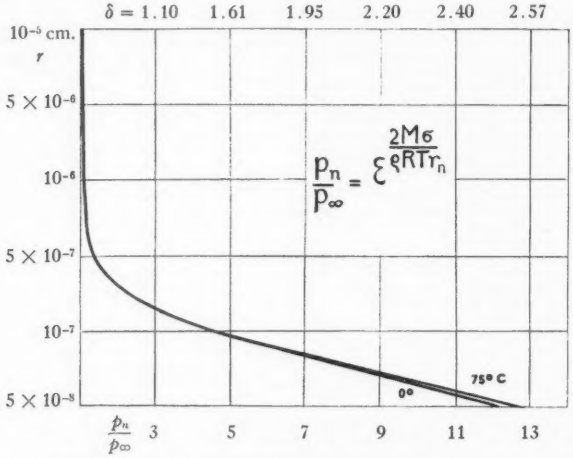

FIG. 1. *Ratio (p_n/p_∞) between the vapour pressure of small drops of water to that of large drops at 75° C. and at 0° C. as a function of the radius r.*

the expansion the ratio $p(n)/p_\infty$ is small, so that equilibrium between the drops and the steam could exist only for large values of r_n, but since large drops have to start as small aggregates of molecules, at least in the absence of dust or ions, condensation depends not only on the degree of undercooling $\delta = \ln p(n)/p_\infty$ but also on the rate of growth of the drops. The two resulting opposite effects, the slight undercooling when expansion begins and the high vapour pressure of tiny drops, constitute the basis of the distinction between dry superheated steam and wet superheated steam. On the one hand, steam may be entirely free from water drops but at a temperature lower than that at which steam can exist, at the same pressure, in prolonged contact

with large drops or a pool of water, or it may consist of vapour mixed with small drops but still at a temperature lower than that at which water in a boiler would exert the same pressure.

Since means of proving the presence of very small drops of water in a mass of steam have their limit of sensitivity, there is no sharp distinction between the two types of undercooled steam. In practice, the first sign that undercooling actually occurs in expanding steam has been the observation that the discharge through a steam nozzle with a throat and a divergent portion is greater than the most accurate calculations predict. The formation of small drops is found to exert a marked influence upon the quantity of steam passing each second through such a convergent–divergent or DeLaval nozzle, and a detailed study of the flow enables not only a calculation of the discharge obtained but also of the radius of the drops formed. When condensation occurs during the expansion in the divergent portion of the nozzle, there is an increase in pressure, or at least a halt in the general decrease of static pressure throughout this region. At such a step in the pressure curve, a dense fog of fine water particles is formed, not gradually but with great suddenness. Even when traces of liquid are present in the steam before the dense fog appears, the major condensation occurs rapidly with formation of a mist. These two effects, the condensation and the stop or upward step in the pressure curve—called latent recompression by C. A. Robb, who observed it for the first time (9)—are closely related and furnish information on the size of the drops, as a study of the equation of flow will show.

Equations of Flow and Size of Drops

In the region near saturation, dry undercooled steam flows in the same way as superheated steam, and if p_0 and v_0 denote the pressure and the volume of the steam at the entrance section of the nozzle, and p_s and v_s the corresponding values at any point in the converging portion, or even beyond the throat provided that no condensation has occurred, the isentropic expansion of the steam obeys the equation

$$p_s v_s^{1.316} = p_0 v_0^{1.316}.$$

Since the work done in an adiabatic isentropic expansion is equal to the change in enthalpy

$$h_s = h_0 - 0.024 \frac{1.316}{1.316 - 1} (p_0 v_0 - p_s v_s).$$

The values h_s, h_0, v_0 (cc.), and p_s (atm.) are known, and v_s can be calculated from the equation $v_s = v_0 (p_0/p_s)^{0.77}$. It is therefore possible to compute h_s for any value p between the entrance and the condensation zone. Over the small ranges of temperatures considered, the law of ideal gases may be applied to obtain T_s. Thus all the properties of the supersaturated or undercooled steam can be obtained, in particular the values h_s and v_s associated with the conditions just before the first signs of condensation.

Beyond the point where the pressure has fallen to p_c, condensation begins and rapidly reaches its peak within the short distance of about 1 cm. When losses are disregarded, it is possible to use the relations represented by the equation of continuity of flow, conservation of energy, and conservation of momentum to compare the properties of the steam at s with those of the steam at c, about 1 cm. upstream from s.

The equation stating continuity of mass flow indicates that

$$\frac{A_c V_c}{v_c} = \frac{A_s V_s}{v_s} = w,$$

where A denotes the area of cross-section and V the velocity of the steam. In the region under consideration $A_s = A_c$, at least approximately.

According to the principle of the conservation of energy

$$Jh_s + \frac{V_s^2}{2g} = Jh_c + \frac{V_c^2}{2g},$$

if by total energy is meant the sum of the kinetic energy plus the total heat h_s per unit mass, both quantities being expressed in the same units. An increase in the value of h between s and c involves a decrease in the speed.

The equation expressing conservation of momentum is

$$w\frac{V_s}{g} + p_s A_s = w\frac{V_c}{g} + p_c A_c,$$

or when the length of the condensation zone is not negligible, and the increase in pressure caused by latent recompression is linear (3),

$$\frac{w}{g}(V_s - V_c) = p_c A_c - p_s A_s - \frac{p_s + p_c}{2}(A_c - A_s).$$

If p_s is directly measured, h_s and v_s can be computed or taken from the steam tables while V_s is deduced from the total heat h_s. Four unknowns—p_c, v_c, h_c, and V_c—remain therefore in the three equations. Measurement of p_c is difficult, because in the zone of condensation the pressure varies, particularly when the ratio p_s/p_0 is changing at a rapid rate immediately before the beginning of condensation. A fourth relation between the unknowns is obtained, however, by introducing the Kelvin–Helmholtz equation. Since drops consisting of only a few molecules have such a high vapour pressure that they can never be in equilibrium with expanding steam for the degrees of undercooling obtainable in practice at the beginning of the expansion, and the larger drops exert the same vapour pressure as a pool of water, a stage must occur during condensation at which the vapour pressure of the drops is equal to the pressure of the surrounding steam and obeys, therefore, the Kelvin–Helmholtz equation. The simplest assumption is that when the first signs of condensation appear either in the rate of the pressure drop along the path of the expanding steam or in the light scattering property of the steam, the first persistent centres are in equilibrium with the surrounding vapour pressure.

The centres of condensation keep increasing in size, of course, otherwise they would never produce a marked optical effect, and if the different vapour pressures computed for different sizes of the drop are introduced into the main equations, it is possible to find the radius at which the system of equations is satisfied when p_c is equal to the highest pressure reached in latent recompression, that is, when condensation is more or less complete.

In the application of the Kelvin–Helmholtz formula attention must be paid, however, to the increase in the density of the water contained in the small drops. Owing to the surface tension of the liquid, the capillary pressure in atmospheres per square centimetre of surface area on a droplet of radius r cm. with surface tension σ dyne per cm. is

$$p = \frac{2\sigma}{r}.$$

Using a value of 75.6 dynes per cm. for water at 0° C., the pressure inside a droplet of 5×10^{-8} cm. radius is 3060 kgm. per sq. cm. When water is subjected to such a pressure, its specific volume is reduced to 0.975 and the radius computed from the degree of undercooling is slightly increased unless the surface tension is affected to the same extent.

Were it not for the uncertainty in the extrapolation of the densities at high pressures, and the lack of knowledge as regards the surface tension of compressed water, the study of the flow of steam through DeLaval nozzles would provide a means for the accurate determination of the size of the droplets formed when sudden condensation occurs, whether the drops consist of a few or of thousands of molecules, that is, whether the radius of the drop is as small as 5×10^{-8} cm. or as large as 5×10^{-4} cm. Water drops of 5×10^{-4} cm. radius or larger drops exert the same vapour pressure as large bodies of water, so that the method is no longer useful when the dimensions have become equal to the wave-length of visible radiation.

Size of Drops Deduced from Tests

In the most recent studies the flow of steam through convergent–divergent nozzles was analysed in sufficient detail to enable at least the determination of the approximate size of the water drops formed at the onset of recompression.

In one set of measurements (3), the pressure at the nozzle entrance was kept between 1.42 and 1.44 atm. abs., the temperature varying between 113.4° and 162.6° C. At the lowest temperature the steam was not far from saturation and started to condense after a short expansion at relatively high pressures, 0.7 atm. abs. When superheated steam was admitted, the pressure had to be reduced to about $\frac{1}{3}$ atm. before recompression—by about 0.07 atm.—and condensation took place. The temperature at which the first sign of latent recompression occurred was calculated from the equation for adiabatic changes,

$$T_c = T_0 \left(\frac{p_c}{p_0}\right)^{\frac{\gamma-1}{\gamma}}.$$

It varied from 53.3° C. at the higher condensation pressures to 41.7° C. for strongly superheated steam. The supersaturation ratio $S = p(n)/p_\infty$ decreased from about 5 at the higher temperatures to 4 at the lowest temperature. The radius calculated from the supersaturation ratios varied from 5.7×10^{-8} to 6.9×10^{-8} cm. Such drops contain from 30 to 60 molecules.

In another series of investigations (14) the effect of variations in the initial conditions of the expanding steam upon condensation pressure and supersaturation was investigated by measuring the static pressure at the condensation point for initial pressures as high as 7 atm. abs. at 188.3° C., near the entrance to the nozzle, and outlet or back pressures varying from 1.16 to 3.06 atm. abs. Pressures at condensation ranged from less than 0.7 to over 3.4 atm. abs.; the computed temperatures at compression were between 37.8° and 93.4° C. When the value of S is calculated and introduced into the Kelvin–Helmholtz equation, the results for the radius vary between 4.5×10^{-8} cm. at the lower temperatures to 6×10^{-8} cm. at the higher temperatures. The smaller radius is considered to be $3\frac{1}{3}$ times as large as that of a single molecule. Recompression, by the way, is distinct only when the nozzle discharges into a space with a relatively high vapour pressure. When the back pressure is less than half the initial pressure there is merely a halt in the expansion curve.

A third investigation on undercooling in steam nozzles had for its object the study of the influence of rough walls upon steam flow and condensation (8). The roughness consisted of dents made in the wall by means of a cape chisel. Four double series of tests were made on four nozzles with smooth, and four nozzles with rough, walls, using inlet pressures of 3, $3\frac{1}{3}$, $3\frac{2}{3}$ and 4 atm. abs., and back pressures of 2.23, 2.37, 2.56, and 2.70 atm. abs. The temperatures at the inlet ranged, accordingly, from 145.6° to 149.4° C. At the condensation point they were 91.3°, 79.3°, 75.9°, and 70.5° C. In each test a first halt in the graph representing pressure as a function of distance from the inlet was found at 1.7 atm. below the inlet pressure. Here a preliminary condensation occurred, the latent recompression amounting to about 1/15 atm.; then the expansion continued until the pressure had decreased an additional $\frac{2}{3}$ atm. At this point, recompression started and continued until the back pressure was reached.

Roughness of the walls caused a retardation of the flow; condensation began at a higher pressure and lower temperature, that is, farther downstream than when the walls are smooth. The radius of the droplets formed in the smooth nozzle was found to be 6.4×10^{-8} cm., at the beginning of latent recompression, whilst the droplets in the rough nozzle had a radius of 7.4×10^{-8} cm.

Other, though less complete, tests revealed the influence of temperature upon supersaturation and drop size (6, 7). When expansion was caused by the rapid displacement of a small piston, the values of $S = p(n)/p_\infty$ and r were as follows:

T_c, °C.	−16.4	3.2	19.1	47
S	7.8	5.1	3.74	2.87
$\delta = \ln S$	2.05	1.69	1.32	1.05
σ	80	75	73	68
$10^8 r$	6.6	6.9	8.3	8.7

These results were obtained when the water vapour was mixed with an excess of air, and the piston travelled a distance of about 2 cm.

More thorough tests on the supersaturation of water vapour in the presence of carefully filtered air were performed at and below room temperature (11). The mixture was contained in a flask holding 0.7 litre, closed by a stopcock with wide bore (1 cm.) and supported inside a thermostat. Rotation of the stopcock connected the flask with a partially evacuated container of 12 litres capacity. The expansion was completed within 0.1 sec., and the pressure then remained constant for 0.3 sec. Ions were removed by applying a potential of 50 volts per cm. to silver coatings on the inner wall of the flask. It was found that down to temperatures of −62° C. the condensation cloud appeared when the supersaturation had reached the degree given by the equation

$$\delta = \ln \frac{p(n)}{p_\infty} = \frac{780}{T} - 1.521.$$

The radius of the condensation centres increases, therefore, in these tests from 8.8×10^{-8} cm. at −20° C. to 10.2×10^{-8} cm. at 50° C., when changes in the density of liquid water are disregarded.

Theoretical Rate of Condensation

All the large water drops start as aggregates of a few molecules, and increase in size mainly by the addition of single molecules. On the average each water molecule would be making 10^{10} collisions per sec. at normal pressure and temperature, and among these will be triple and a few other multiple collisions. Owing to the Maxwellian distribution of the velocities, a few molecules may succeed in maintaining the growth of the water drops by themselves performing the work to be done against the surface tension. In view of the large number of collisions, drops of different sizes will be formed when the temperature of the steam is lowered and condensation is rendered possible. The question is whether the number of the larger drops will be appreciable or whether the condensation will be too slow to be measured (2, 4).

Let it be assumed that in the early stages of undercooling when the steam exerts the pressure $p(n)$, there are $N(\nu)$ drops per cc. with exactly ν molecules each and a vapour pressure $p(\nu)$, $N(\nu + 1)$ drops with $(\nu + 1)$ molecules and the vapour pressure $p(\nu + 1)$, and so on. Drops for which $p(\nu) = p(n)$ are in equilibrium with the surrounding steam, that is, they receive on the average as many molecules from the vapour as they lose to the vapour by evaporation. Smaller drops have a vapour pressure greater than $p(n)$ and

tend to lose molecules. For larger drops the vapour pressure approaches the value p_∞, so that more molecules are retained than lost. The reduction in vapour pressure that is brought about by the increase in the size of the drops renders possible the continued growth of some drops. Slight as the probability may be for the smaller particles not to disintegrate, relatively few nuclei of condensation, 10^6 to 10^8, suffice to produce a noticeable effect, and a certain number C of aggregates of molecules keep adding molecule after molecule. The task now is to determine the rate at which molecules are retained, for the number C must be equal at each stage to the number of particles that receive in a given time one water molecule more than they lose.

For the vapour surrounding the drops, the number of molecules traversing unit surface during each second is $a_0 p(n)$; the number impinging upon $N(\nu)$ particles is therefore $a_0 p(n) N(\nu) F(\nu)$, where $F(\nu) = 4\pi r_\nu^2$ is the surface of one particle. During the same time $a_0 p(\nu + 1)\ N(\nu + 1)\ F(\nu + 1) = a_0 p(\nu + 1) S_{\nu+1}$ molecules leave the surface of the drops of next larger size. The symbol $a_0 S_1$ denotes the number of collisions that a molecule makes each second with molecules of the same kind when the pressure is equal to unity (4):

$$a_0 = \frac{N}{\sqrt{2\pi MRT}}.$$

To maintain the rate of condensation at a level of C drops per second, it is necessary that in the steady state C satisfies the equations

$$\begin{cases} C = a_0 p(n) S_\nu - a_0 p(\nu + 1) S_{\nu+1} \\ C = a_0 p(n) S_{\nu+1} - a_0 p(\nu + 2) S_{\nu+2} \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ C = a_0 p(n) S_s - a_0 p(s) S_{s+1} \end{cases}$$

or is larger than these relations indicate. Multiplication of the second equation by $p(\nu + 1)/p(n)$, of the third by $p(\nu + 1)p(\nu + 2)/p^2(n)$, and so on, of the last one by $p(\nu + 1)p(\nu + 2) \ldots p(s)/p^s(n)$, and addition on each side of all the expressions thus obtained gives

$$\left(1 + \frac{p(\nu+1)}{p(n)} + \frac{p(\nu+1)p(\nu+2)}{p^2(n)} + \ldots + \frac{p(\nu+1)p(\nu+2)\ldots p(s)}{p^s(n)}\right) C = a_0 p(n) S_\nu - a_0 p(s) S_{s+1}.$$

The letter s indicates the number of steps occurring in the growth of each drop. It has to reach large values because in order to produce noticeable scattering at right angles to a beam of light traversing the vapour, the radius r must not be very small with respect to the wave-length of visible radiation, $\lambda = 0.5 \times 10^{-4}$ cm. approximately, and when $r = \lambda/20$, the drop contains about one million molecules. The number of the drops, however, need not be large, and since $p(s)$ is at any rate smaller than the pressure, $p(n)$, near the onset of condensation, the term $a_0 p(s) S_{\nu+1}$ is negligible in comparison with $a_0 p(n) S_\nu = a_0 p(n) N(\nu) F(\nu)$, provided ν is taken sufficiently small, for instance, equal to unity. In flowing steam the larger drops are removed as

fast as they are formed. Starting from single molecules ($\nu = 1$), the condensation per second is therefore measured by

$$R'C = a_0 p(n) N(1) F(1) = a_0 p(n) S_1$$

or

$$\ln C = \ln a_0 p(n) S_1 - \ln R'.$$

For the condensation to become visible, the difference between the natural logarithms must attain at least 10, if C is to exceed 22,000 per sec.

The product $a_0 p(n)\ N(1)\ F(1)$ is equal to the number of collisions occurring per second in unit volume between steam molecules at the pressure $p(n)$. When v is the average velocity of the molecules at the temperature T, l the mean free path at the pressure $p(n)$, v_0 and l_0 the corresponding values at 0° C. and atmospheric pressure, the number of collisions per second per cubic centimetre is given by $N(1)v/l$, or

$$a_0 p(n) N(1) F(1) = N(1)v/l = N^2(1)v/l_0 N = N \sqrt{\frac{8}{\pi R}} \frac{T_0}{p_0 l_0} \frac{1}{\sqrt{M}} \frac{p^2}{T\sqrt{T}}$$
$$= \frac{5 \times 10^{22}}{l_0 \sqrt{M}} \frac{p^2}{T^{3/2}},$$

where $N = 6.023 \times 10^{23}$ (Avogadro's number), and p is expressed in millimetres of mercury. The vapour pressure of the small nuclei of condensation at the moment of their formation may be considered as at least equal to the pressure $p(1) = p_e$ of the surrounding steam. Values obtained on this assumption for the number of collisions at different temperatures are given in Table I, side by side with the natural logarithms of the numbers. The number is approximately trebled by each increase of 10° C. in the temperature of the vapour; to obtain C it must be divided by R'.

TABLE I

NUMBER OF COLLISIONS AND SURFACE WORK AT VARIOUS TEMPERATURES

t, °C.	$a_0 p(1) S_1$	$\ln a_0 p(1) S_1$	$\sigma F(n)/3kT$				$2\sigma F(n)/3kTn^{2/3}$
			$n = 27$	64	125	216	
0	1.37×10^{24}	55.375	28.2	50.2	78.4	112	6.275
10							
20	1.79×10^{25}	58.381	25.3	45.0	70.3	101	5.625
30	5.65×10^{25}	58.881	24.0	42.6	66.6	96	5.325
40	1.62×10^{26}	60.679	22.7	40.3	62.9	91	5.04
50	4.33×10^{26}	61.521	21.4	38.1	59.5	86	4.76
		Max. $\sum_2^s \left(\frac{1}{\nu^{1/3}} - \frac{1}{s^{1/3}}\right)$	$\doteqdot$	5.6	10.1	51.6	

As regards the value of R', since

$$\frac{p(\nu+1)}{p(n)} = \epsilon^{-\frac{2}{\rho}\frac{\sigma M}{RT}\left(\frac{1}{r_n} - \frac{1}{r_{\nu+1}}\right)} = \epsilon^{-\frac{2\sigma M}{\rho R T r_n}\left(1 - \frac{r_n}{r_{\nu+1}}\right)}$$

and the mass of a drop with ν molecules equals

$$\frac{4\pi}{3}\rho r_\nu^3 = \nu\frac{M}{N}$$

or

$$\frac{r_\nu^3}{\nu} = \frac{3}{4\pi\rho}\frac{M}{N}$$

$$\frac{r_\nu}{r_{\nu+1}} = \frac{\nu^{1/3}}{(\nu+1)^{1/3}},$$

the sum for R' becomes

$$R' = 1 + \epsilon^{\frac{2\sigma M}{\rho RT}\frac{n^{1/3}}{r_n}\left(\frac{1}{2^{1/3}}-\frac{1}{n^{1/3}}\right)} + \epsilon^{\frac{2\sigma M}{\rho RT}\frac{n^{1/3}}{r_n}\left(\frac{1}{2^{1/3}}+\frac{1}{3^{1/3}}-\frac{2}{n^{1/3}}\right)} + \ldots + \epsilon^{\frac{2\sigma M}{\rho RT}\frac{n^{1/3}}{r_n}\left(\frac{1}{2^{1/3}}+\cdots\frac{1}{s^{1/3}}-\frac{s-1}{n^{1/3}}\right)}.$$

When the numerator and the denominator of $2\sigma Mn^{1/3}/(\rho RTr_n)$ are multiplied by the surface area $F(n) = 4\pi r_n^2$ of the equilibrium drop with n molecules, the relation

$$\frac{2\sigma M}{\rho RT}\frac{n^{1/3}}{r_n} = \frac{2\sigma F(n)}{3kTn^{2/3}}$$

is obtained. The value of $2\sigma F(n)/3kTn^{2/3}$ decreases with increasing temperature but is independent of n or r (Table I) since

$$\frac{4\pi r_n^2\sigma}{3kTn^{2/3}} = \frac{4\pi\sigma}{3kT}\left(\frac{r_n}{n}\right)^{2/3} = \frac{8\pi\sigma}{3kT}\left(\frac{3M}{4\pi\rho N}\right)^{2/3}.$$

As regards the differences $1/\nu^{1/3} - 1/n^{1/3}$, they are positive so long as the drop contains fewer molecules than would be required to bring it into equilibrium with the surrounding vapour pressure $p(n)$, which is thought to be maintained at this value by a constant supply of steam. The sums of $(\nu^{-1/3} - n^{-1/3})$ in the first few brackets are small; the ones that follow increase to a maximum for $\nu = n$, that is, when equilibrium has been reached, then they decrease to zero for $\nu \doteqdot 3n$, and change finally to negative values. The first terms in the series for R' are therefore relatively small, and the uncertainty in the value to be used for the vapour pressure of aggregates of a few molecules does not interfere with the application of the theory. On the other hand, when $s = n$, and n exceeds 30, the sum of the fractions $2/3\,\nu^{-1/3}$, where ν has values from 2 to n, is equal to $n^{2/3} - 2^{2/3}$, and the maximum is

$$\frac{1}{2^{\frac{1}{3}}} + \frac{1}{3^{\frac{1}{3}}} + \frac{1}{4^{\frac{1}{3}}} + \ldots + \frac{1}{n^{\frac{1}{3}}} - \frac{n-1}{n^{\frac{1}{3}}} = \frac{n^{2/3}}{2} - 2.3811 + n^{-1/3}.$$

Should the degree of undercooling be small, and therefore the equilibrium drop large, the term for $s = n$ in the series determining R' is alone greater than $a_0p(1)S_1$; hence C is smaller than unity, and condensation negligible (Table I, last line, and note added on page 94).

More accurately, when the number of molecules contained in the equilibrium drop is so large that the general term a_s in the series Σa_s for R'

$$a_s = \epsilon^{\frac{\sigma F(n)}{3kT}\frac{2}{n^{2/3}}\left(\frac{1}{2^{1/3}}+\frac{1}{3^{1/3}}+\cdots+\frac{1}{s^{1/3}}-\frac{s-1}{n^{1/3}}\right)}$$

may be written

$$a_s = \epsilon^{\frac{\sigma F(n)}{3kT}\frac{2}{n^{2/3}}\left(\frac{3}{2}s^{4/3} - \frac{3}{2}2^{2/3} - \frac{s-1}{n^{1/3}}\right)}$$

or

$$a_s = \epsilon^{\frac{\sigma F(n)}{3kT}\left(\frac{2}{n} - 3\frac{2^{2/3}}{n}\right)} \epsilon^{\frac{\sigma F(n)}{3kT}\left(3\left(\frac{s}{n}\right)^{2/3} - 2\left(\frac{s}{n}\right)\right)},$$

the sum Σa_s, with the exception of the first and negligible terms of the series, is given by the integral

$$3n\epsilon^{\frac{\sigma F(n)}{3kT}\left(\frac{2}{n} - 3\frac{2^{2/3}}{n}\right)} \int x^2 \epsilon^{\frac{\sigma F(n)}{3kT}(3x^2 - 2x^3)}\, dx,$$

where

$$0 < x = \left(\frac{s}{n}\right)^{1/3} < \infty \quad \text{and} \quad ds = 3nx^2dx.$$

The steady rate of condensation can thus be written

$$C = \frac{a_0 p(1)\, N(1)\, F(1)}{R_I}\, \epsilon^{-\frac{\sigma F(n)}{3kT}},$$

where for values of n larger than about 500

$$R_I = 3n \int_0^\infty x^2 \epsilon^{\frac{\sigma F(n)}{3kT}(3x^2 - 2x^3 - 1)}.$$

The integrand is represented in Fig. 2 for ratios of $\sigma F(n)/3kT$ ranging from 20 to 50, that is, for increasing temperatures (Table I).

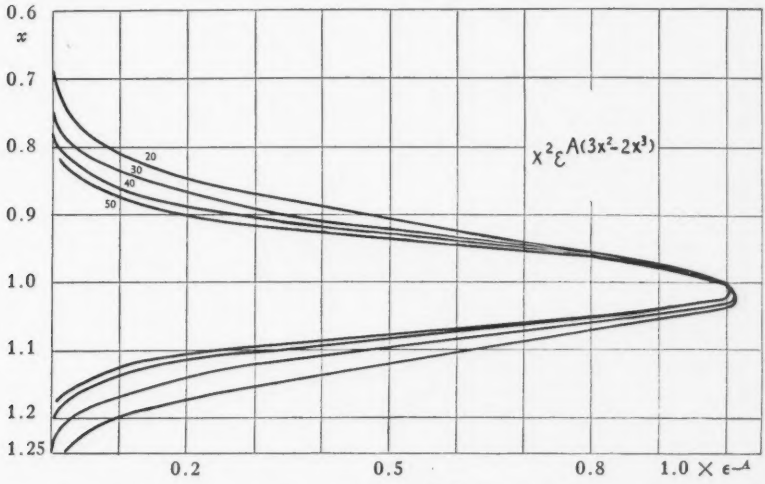

FIG. 2. *Curves representing the function* $x^2\epsilon^{A(3x^2-2x^3)}$ *for values of* x *between 0.6 and 1.25 and* $A = \sigma F(n)/3kT$ *between 20 and 50.*

In the modified formula for C the fraction appearing before the exponential function is practically independent of the size of the drops provided that they are larger than the condensation centres. The exponential function recalls

the expression for the influence of height upon the distribution of molecules or colloidal particles subjected to gravity, the work $\sigma F(n)$ appearing in place of the work required to lift a particle to a given level. The sum R_1 depends on the temperature and corrects for the absence of equilibrium between the pressure of the vapour and the vapour pressure of drops of different sizes. The product on which it depends,

$$x^2\exp(3x^2 - 2x^3 - 1)\sigma F(n)/3kT\,,$$

has a maximum for

$$x^3 - x^2 - kT/\sigma F(n) = 0\,,$$

or for

$$x = \frac{2}{3}\cosh\frac{u}{3} + \frac{1}{3}\,,$$

where

$$\cosh u = 1 + 9\frac{3kT}{\sigma F(n)}\,.$$

As $\sigma F(n)/3kT$ changes from 10 to 50, the maximum decreases slightly, from about 1.02 to 1.0, and shifts from $x = 1.06$ to $x = 1.01$. The value of R_1 is at the most equal to n, since the area defined by the vertical x-axis and the curve x^2 exp. $(3x^2 - 2x^3 - 1)\sigma F(n)/3kT$ is approximately a triangle with height 1 and base smaller than 1 (Fig. 2). It need not be computed with great accuracy as long as the smallest value of C that the methods of observation are able to detect is known only to within the order of magnitude. The theoretical value of C is computed from

$$\ln C \doteq \ln a_0 p(n) S_1 - \sigma F(n)/3kT + \ln n.$$

It may be added that since for particles that are in equilibrium with the surrounding vapour

$$\frac{\sigma F(n)}{3kT} = \frac{4\pi}{3}\frac{N\sigma}{RT}\left(\frac{2\sigma M}{\rho RT\delta}\right)^2$$

and

$$n = \frac{4\pi}{3}\rho\frac{N}{M}\left(\frac{2\sigma M}{\rho RT\delta}\right)^3,$$

the fraction $\sigma F(n)/3kT$ is also equal to $n\delta/2$, and the equation for the rate of condensation becomes

$$C = \frac{a_0 p(1) N(1) F(1)}{R_1}\,\epsilon^{-\frac{n\delta}{2}} = \frac{a_0 p(1) N(1) F(1)}{R_1}\,\epsilon^{-\frac{\sigma M}{\rho RT}\left(\frac{4\pi\rho}{3}\frac{N}{M}\right)^{1/3} n^{2/3}}$$

In this form the retarding influence of a large value of n in the exponential function appears more clearly.

Application

It is evident, therefore, that drops with a radius exceeding 10^{-7} cm. are not acting as centres of condensation. This conclusion is valid, of course, only for spontaneous condensation of undercooled water vapour. When ions or fine dust particles, recently rendered visible by the electron microscope, are present, and serve as nuclei of condensation, the formation of minute drops

is by-passed and the large terms in the series for R are eliminated, the smallest value of ν being much greater than n. But in the absence of ions or impurities, the most difficult stage in the condensation of water is the formation of small drops having a vapour pressure two or three times higher than that exerted by the undercooled vapour, and it is natural that the greater the difference in the size of the drops at equilibrium and the size of the drops first formed—which consist necessarily of few molecules—the more unlikely it is that condensation by undercooling will succeed (Fig. 1). The number of drops formed by slight undercooling is insignificant. According to the calculation for C the limit is reached when more than a hundred molecules are required to build up the equilibrium drop (Table I). This result is in good agreement with the values reported in the various investigations mentioned. Despite the considerable variations in the conditions of the tests, the radius of the drops, acting as centres of condensation, invariably range from 4.5×10^{-8} cm. to about 9×10^{-8} cm. at the most. Hence the largest drops found to be active as centres of condensation do not contain more than about 100 molecules.

As regards the influence of temperature, the theory indicates that the same number of drops is formed at a lower degree of undercooling when the temperature at which condensation occurs is increased. In other words, at higher temperatures larger drops form and promote condensation as much as small drops. An examination of the radius determined from the tests on flowing steam leaves no doubt that this conclusion is correct (Fig. 3). There is a distinct trend toward larger values of r_n when the temperature of condensation increases from 40° to 90° C. in the steam flow tests or from −16° to 50° C. in the cloud chamber experiments.

For all except the largest nuclei of spontaneous condensation, the values obtained for the number C of drops formed per second is so large that a very short time, not much more than a few micro-seconds, is sufficient for the formation of thousands of drops and the development of a cloud of water particles. Now the solution of the equations of flowing steam gives the speed of flow V and hence the time taken by the steam to traverse the space between the point where the first sign of condensation appears and the point where latent recompression has reached its peak. In convergent–divergent channels the corresponding distance is about 1 cm. Determinations from four tests in which the initial pressures were as far as possible the same, 1.43 to 1.44 atm. abs., and the initial temperature varied only between 137.5° and 141.5° C., give the four values 17, 21, 25, or 21 micro-seconds (3). In the comparison between nozzles with smooth and those with rough walls the time elapsed after the expanding steam passes the saturation stage until it undergoes condensation is 37 micro-seconds in the smooth channel and 47 micro-seconds in the rough channel.

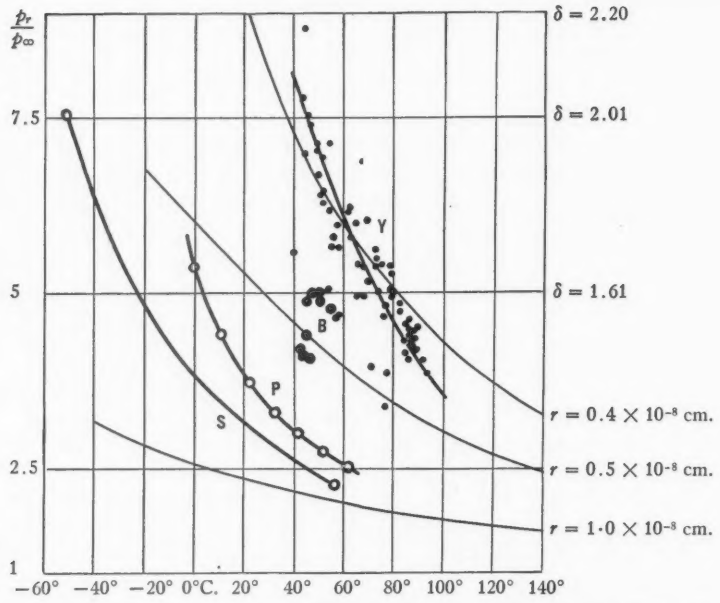

FIG. 3. *Radius of small water drops condensing at various temperatures for various degrees of supersaturation S or δ = lnS = ln (p_r/p_∞). The curves in light lines indicate constant radius despite changing temperature; those in heavy lines connect values deduced on the assumption that the Kelvin–Helmholtz equation applies when the first visible signs of a cloud of condensing drops appear. At one and the same temperature, condensation in air (Curves P and S—Powell (7) and Sander (11)) appears to occur with less undercooling than in pure steam (Curve Y—Yellot (14) and group at B—Binnie (3)), but perhaps only because it is easier to detect under stationary conditions.*

Size of Drops and Scattering of Light

In nozzles in which the throat that connects the convergent passage with the divergent part is of negligible length, condensation appears as a blue mist, and the blue colour is maintained throughout the length of the jet. The light scattered at right angles to the incident beam is completely plane-polarized, and the intensity of the light scattered in other directions is symmetrical with respect to the perpendicular to the beam. Colour and polarization are evidence of small droplet size ranging in radius from a negligible fraction of the wave-length of light to as much as one-tenth of the wave-length in the red (10). An accurate determination of the size would be possible if the number of particles were known. Hints that the largest possible size is the correct choice are given by the tests with longer throats and increased outlet pressures (14).

Latent recompression can indeed be reduced to a negligible amount by changing the trumpet-like shape of the DeLaval nozzle to a more cylindrical form, with a long throat and a gradual widening at each end. If steam expands through such a channel without condensation against a low back

pressure, the pressure drop per unit length is practically constant at all points. When the initial conditions of the steam are the same as in the comparison between convergent–divergent nozzles with either smooth or rough walls (4.06 atm. abs. and 151.7° C. at the inlet), there is observed a slight flattening of the rate of drop in two sections of the channel, about $2\frac{1}{2}$ cm. apart, where the liberation of heat of condensation tends to raise the pressure (8). In a strong beam of light sent through the nozzle a slight bluish haze of scattered light indicates preliminary condensation at the section nearer to the entrance ($p_c = 2.2$ atm., $t_c = 98.6°$ C., computed, $V_c = 341.8$ m. per sec.), whereas at the second cross-section a darker blue colour reveals ultimate condensation. After the blue colour come yellow, orange, and red. This sequence of colours along the tube reveals that the drops continue to increase in size when a long throat retards the rapidity of expansion. The complete absence of violet, even in preliminary condensation, convincingly proved by photography, shows, moreover, that the particles seen are never very much smaller than the wave-length of visible radiation. Evidently the centres of condensation add quite rapidly to their size until dimensions comparable with the wave-length of light are attained. At this stage the colours of the scattered light are very sensitive to slight changes in the conditions of the steam; they vanish when the temperature of the steam is raised but slightly (8, 14).

Could the increase in the size of the drops be relied upon to continue indefinitely at the rate it had during the growth of small nuclei to particles of one micron diameter, the presence of a single drop visible to the naked eye would serve as the first indication that condensation had occurred. Under these conditions, C would be equal to unity and $a_0 p(n) S$ equal to R.

Amount of Work Done Against the Surface Tension

An increase in the temperature T_c of a drop, due to the retention of the latent heat yielded by condensing molecules, counteracts the reduction in the vapour pressure that accompanies the increase in radius, and lowers therefore the chance for the particle to acquire molecule after molecule.

Should the increase in the temperature of the drop caused by condensing molecules, which at the same time increase the radius r by dr, be equal to the change in temperature that would lead to the same reduction in the relative vapour pressure of the drop as the increase in radius, the end of that part of the condensation that is possible without heat transfer would be reached. Let the latent heat of condensation at the temperature T_c°K. (or t° C.) be λ_c cal. per gm. and c the specific heat of the liquid; the temperature increases with the radius r at the rate

$$\frac{dT}{dr} = \frac{3\lambda_c}{rc} = \frac{3}{rc}(594.4 - 0.51t)$$

for water. Now the differentiation of the Kelvin–Helmholtz equation at the equilibrium temperature with respect to r gives, when the vapour pressure p_c of the surrounding steam is maintained,

$$-\frac{dT}{dr}\left(\frac{T}{p_\infty}\frac{dp_\infty}{dT}-\ln\frac{p_c}{p_\infty}\right)=\frac{2\sigma M}{\rho R r^2},$$

provided that σ/ρ remains constant. Or, since, according to the approximate equation by Clausius and Clapeyron

$$\frac{dp_\infty}{dT}=\frac{M\lambda p}{RT^2},$$

with λ in ergs equal to $4.186\times10^7\,\lambda_c$, there follows

$$r=\frac{2\sigma}{\rho\lambda}\left(\frac{cT}{3\lambda_c}+1\right).$$

For water, the limiting radius found, 0.5×10^{-8} cm., is too small to play a part in the process of condensation, that is, even the smallest drop must dissipate the heat of condensation if growth is to be maintained. In small drops each additional molecule of water reduces the relative vapour pressure at the rate

$$\frac{d(p_\nu/p_\infty)}{d\nu}=\frac{2\sigma M^2/\rho^2}{75.687\times10^{23}T}\frac{1}{r_\nu^4}\frac{p_r}{p_\infty}=\frac{648}{10^{23}T}\frac{1}{r_\nu^4}\frac{p_r}{p_\infty}.$$

The reduction per molecule is inversely proportional to the fourth power of the radius, whereas the change with temperature at constant p_c

$$\frac{d(p_c/p_\infty)}{dT}=\frac{-2\sigma M}{\rho RT^2 r}\frac{p_c}{p_\infty}$$

is inversely proportional to the radius, and is therefore much smaller. When the amount of heat, equal to $\lambda M/N$, yielded to a drop by the condensation of one molecule, is considered to be similar to a heat of reaction, it increases the temperature of the drop by

$$T-T_0=\frac{\lambda_c}{\nu c}\,^\circ\mathrm{C.}=\frac{594.4-0.51t}{\nu c}\,^\circ\mathrm{C}.$$

As long as the number ν is small, the elevation of temperature is considerable, a few hundred degrees. Before the smallest drop can reach a stable state, it must therefore transfer or radiate the heat gained

$$\lambda_1=9.329\times10^{-13}-6.817T\times10^{-16}\text{ in ergs per molecule}$$

to the surrounding medium, or use it up in the performance of mechanical work. The fraction of the heat that can be transformed continuously into useful work is on the average equal to $(T_a-T_c)/T_a$, where T_a is the absolute temperature of the drop and T_c that of the surroundings. Hence the smaller the drop the greater is the fraction of the latent heat likely to prove useful in overcoming the surface tension. This circumstance aids in the formation of the smallest drop but does not influence the theoretical result, which is determined essentially by the addition of molecules to drops approaching the equilibrium size.

Introduction of the values of ν or n into the formula expressing the work to be performed against the surface tension during the formation of a drop with radius r and ν molecules gives (10)

$$dA = \sigma\left(8\pi r - 8\pi\frac{r^2}{r_n}\right)dr$$

$$\frac{dA}{d\nu} = 6\left(\frac{4\pi}{3}\right)^{1/3}\left(\frac{M}{\rho N}\right)^{2/3}\frac{\sigma}{\nu^{1/3}} - \delta\frac{kT}{2},$$

$$= 1.396 \times 10^{-15}\left(\frac{M}{\rho}\right)^{2/3}\frac{\sigma}{\nu^{1/3}} - 1.3805\,\delta\frac{T}{2} \times 10^{-16}$$

$$\frac{dA}{d\nu} = 2.104 \times 10^{-15}\frac{\sigma}{\nu^{1/3}} - 0.69 \times 10^{-16}\delta T$$

per condensing molecule,

where σ is about 75 and δ normally between 1 and 2 (Fig. 4).

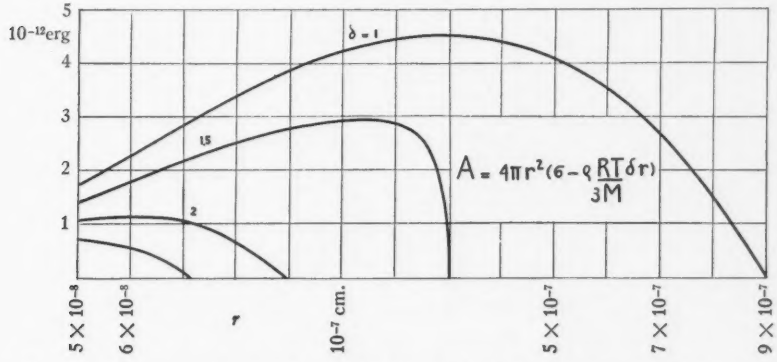

FIG. 4. *Work required against the surface tension σ during the formation of small drops of water of radius r at various degrees of supersaturation $\delta = ln\ (p_r/p_\infty)$.*

It will be seen that even if only a fraction of the heat of condensation λ_1 is used in the early stages in the work against the surface tension, the formation of stable small drops is assured.

Undercooling of Small Water Drops

When condensation is induced at higher temperatures, smaller degrees of undercooling are able to maintain the formation of drops, and the size of the equilibrium drops increases. Near the critical temperature the radius of the drops formed is comparable to the wave-length of light, and even the first traces of condensation become noticeable as opalescence in the absence of any growth in the size of the particles.

When on the contrary the expansion of the water vapour occurs near room temperature, condensation takes place below the freezing point of water. There is, however, no formation of ice crystals, probably in part on account

of the high pressure exerted upon the contents of the small drop by the surface tension, 75.5 dynes per cm. at 0° C. and approximately 80 dynes per cm. at −20° C. Since this pressure is equal to

$$P = \frac{2\sigma}{r},$$

it amounts at 0° C. to 3,060 kg. per sq. cm. when the radius is equal to 5×10^{-8}cm., 306 kg. per sq. cm. when the radius is 5×10^{-7} cm., and so on. At the highest pressure, water is not only liquid down to −18° C. but would form the III′ modification of ice instead of ordinary ice should freezing occur (12, p. 158). At 300 kg. per sq. cm., water remains liquid until the temperature has decreased to less than −2.5° C.

Acknowledgment

This contribution was rendered possible by the clear and complete reports published and discussed in detail by previous investigators in the Transactions of the American Society of Mechanical Engineers and in the Proceedings of the Institute of Mechanical Engineers.

Note Added to Page-proof. Multiplication of all the terms a_s by ϵ^{-A}, where $A = \sigma F(n)/3kT$, and addition of all the products obtained give the value of R_1 directly, and furnish a verification of the accuracy of the integration method used on page 87 for a finite number n of molecules. For $n = 64$ and $A = 32$, constants corresponding to a temperature of 70° C., R_1 is equal to 0.05 and its natural logarithm to −2.71. In the expressions determining C according to the formula $\ln C = \ln a_0 p(n) S_1 - \sigma F/3kT + \ln R_1$ the numerical value obtained for R_1 represents only a correction whose importance is lessened by the uncertainty in regard to the smallest number of particles that the measuring methods used can detect. Near 10° C., the logarithm is increased to about −6.3. For $n = 125$ and 40° C., with $A = 62.5$, the sum for R_1 is equal to 0.0105 and the logarithm to −4.55 so that condensation at this temperature is likely to occur at a measurable rate although the difference $\ln a_0 p(n) S_1 - \sigma F/3kT$ is negative.

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